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Rhenium–osmium systematics of calcium–aluminium-rich inclusions in carbonaceous chondrites

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Abstract—The Re–Os isotopic systematics of calcium–aluminium-rich inclusions (CAIs) in chondrites were investigated in order to shed light on the behavior of the Re–Os system in bulk chondrites, and to constrain the timing of chemical fractionation in primitive chondrites. CAIs with relatively unfractionated rare earth element (REE) patterns (groups I, III, V, VI) define a narrow range of $^{187}\text{Re}/^{188}\text{Os}$ (0.3764–0.4443) and $^{187}\text{Os}/^{188}\text{Os}$ (0.12599–0.12717), and high but variable Re and Os abundances (3209–41,820 ppb Os). In contrast, CAIs that show depletions in highly refractory elements and strongly fractionated REE patterns (group II) also show a much larger range in $^{187}\text{Re}/^{188}\text{Os}$ (0.409–0.535) and $^{187}\text{Os}/^{188}\text{Os}$ (0.12695–0.13770), and greater than an order of magnitude lower Re and Os abundances than other groups (e.g., 75.7–680.2 ppb Os).

Sixteen bulk CAIs and CAI splits plot within analytical uncertainty of a 4558 Ga reference isochron, as is expected for materials of this antiquity. Eight samples, however, plot off the isochron. Several possible reasons for these deviations are discussed. Data for multiple splits of one CAI indicate that the nonisochronous behavior for at least this CAI is the result of Re–Os reequilibration at approximately 1.6 Ga. Thus, the most likely explanation for the deviations of most of the nonisochronous CAIs is late-stage open-system behavior of Re and Os in the asteroidal environment.

The $^{187}\text{Os}/^{188}\text{Os}$ –Os systematics of CAIs are consistent with previous models that indicate group II CAIs are mixtures of components that lost the bulk of their highly refractory elements in a previous condensation event and a minor second component that provided refractory elements at chondritic relative proportions. The high Re/Os of group II CAIs relative to other CAIs and chondrite bulk rocks may have been caused by variable mobilization of Re and Os during medium- to low-temperature parent body alteration ~4.5 Ga ago. This model is favored over nebular models, which pose several difficulties.

The narrow range of $^{187}\text{Os}/^{188}\text{Os}$ in group I, III, V, and VI bulk CAIs, and the agreement with $^{187}\text{Os}/^{188}\text{Os}$ of whole rock carbonaceous chondrites suggest that on a bulk inclusion scale, secondary alteration only modestly fractionated Re/Os in these CAIs. The average of $^{187}\text{Os}/^{188}\text{Os}$ for group I, III, V, and VI CAIs is indistinguishable from average CI chondrites, indicating a modern solar system value for $^{187}\text{Os}/^{188}\text{Os}$ of 0.12650, corresponding to a $^{187}\text{Re}/^{188}\text{Os}$ of 0.3964. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

The ^{187}Re – ^{187}Os decay system potentially provides a unique chronometer to obtain absolute age constraints on processes that affected highly siderophile elements (HSE) during early solar system processing. Precise Re–Os ages (± 0.2 – 0.6% , 2σ) obtained on various groups of iron meteorites likely reflect system closure subsequent to metal crystallization in asteroidal cores (Smoliar et al., 1996; Shen et al., 1996). An age of 4558 Ma is assumed for the IIIA iron meteorites based on ^{53}Mn – ^{53}Cr similarities between angrite meteorites and IIIA irons (Lugmair et al., 1992; Nyquist et al., 1994) and the precise ^{206}Pb – ^{207}Pb ages of the angrites (Lugmair and Galer, 1992). This age was used to determine a decay constant for ^{187}Re of $1.666 \times 10^{-11} \text{ a}^{-1}$ (Smoliar et al., 1996). The Re–Os systematics for IIA and IVB irons indicate similar early core segregation and crystallization in asteroids. The inferred IIIA age is only slightly younger than the oldest solar system objects known, Ca–Al-rich

inclusions (CAIs) from the Allende meteorite, dated at 4566 ± 2 Ma, using the ^{206}Pb – ^{207}Pb method (Chen and Wasserburg, 1981; Manhès et al., 1988). The composition of CAIs suggests that these objects formed as early condensates from a hot gas of solar composition (Grossman, 1972; MacPherson et al., 1988). Comparable ages obtained on fragments of evolved asteroids (Lugmair and Galer, 1992; Smoliar et al., 1996; Shen et al., 1996) and CAIs support the notion that the evolution of the early solar nebula from a dust cloud to a proto-planetary system occurred within a few Ma (Weidenschilling, 1988; Wood and Morfill, 1988; Wetherill, 1990).

At the partial pressures of oxygen and hydrogen commonly assumed for the early solar gas, Re and Os behave as highly refractory elements, and should have been among the first elements to condense (Grossman, 1973; Palme and Wlotzka, 1976). Calculations suggest that, at the very reducing conditions present in a hot gas of solar composition ($\text{H}_2\text{O}/\text{H}_2 = 5 \times 10^{-4}$, $f\text{O}_2 = 10^{-15}$ to 10^{-17}), Re and Os have similar 50% condensation temperatures near 1800 to 1900 K, if they condense into a single alloy and show ideal solution behavior (Grossman, 1973; Palme and Wlotzka, 1976; Fegley and

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Palme, 1985; Sylvester et al., 1990). If such conditions prevailed in the early solar system, volatility-controlled Re-Os fractionations in early solar-system condensates require effective separation and isolation of these grains from the gas in a very specific temperature interval (Sylvester et al., 1990). Alternatively, variations in Re/Os of condensates may have been caused by large changes in fO_2 . Variable abundance patterns of siderophile elements in CAIs and their metal components suggest that, at least locally, fO_2 may have been variable in the early solar nebula (Fegley and Palme, 1985). This interpretation has been questioned and parent body alteration has been suggested as an alternative (Wasson and Krot, 1994). Some siderophile elements (e.g., W, Mo, Re) are highly refractory under very reducing conditions but form volatile oxides at higher fO_2 (Fegley and Palme, 1985; Palme et al., 1998). Rhenium and Os may be fractionated from each other more easily at higher oxygen fugacities where Re is more volatile than Os (Palme et al., 1998).

Bulk chondrites show resolvable fractionations in Re/Os (Fig. 1 and Morgan and Lovering, 1967; Morgan, 1985; Meisel et al., 1996; Chen et al., 1998; Walker et al., 2001) that cannot be attributed to metal-sulfide-silicate fractionation, but are likely volatility-controlled (Walker et al., 2001). Two types of apparent Re-Os fractionations have been reported for chondrites. First, bulk rock samples of ordinary and enstatite chondrites tend to have higher present-day Re/Os and $^{187}Os/^{188}Os$ than carbonaceous chondrites (Fig. 1 and Morgan and Lovering, 1967; Morgan, 1985; Meisel et al., 1996; Chen et al., 1998; Walker et al., 2001). The long-term differences in Re/Os among chondrite groups most likely result from chemical differentiation processes (volatility control) in the early solar nebula (Morgan, 1985; Walker et al., 2001). Second, significant deviations of some chondrite samples from the well-defined IIIA iron meteorite isochron have also been noted (Meisel et al., 1996; Walker et al., 2001). Deviations from purported, near primordial isochrons, upon which all chondrites should predictably plot are difficult to explain. Possible explanations for these small-scale deviations include: (1) extreme chemical differentiation processes in the early solar system, (2) primordial Os isotopic heterogeneities in the solar nebula, (3) analytical problems, and (4) late-stage open system behavior, resulting in preferential loss of Re vs. Os or vice versa.

To examine Re-Os fractionations, particularly with respect to their timing, we have initiated detailed Re-Os isotopic studies of chondrite bulk rocks (Walker et al., 2001), and chondrite components such as CAIs, matrix, metal, and chondrules (Becker et al., 1998; Becker et al., 1999). The focus of this contribution is on the Re-Os systematics of CAIs. Although the major and trace element compositions of many CAIs are similar to those expected for nebular condensates, most show evidence for complex histories. For example, many CAIs show textural evidence that they were melted subsequent to formation (Grossman, 1980; MacPherson et al., 1988). In addition, the presence of secondary mineral assemblages in some CAIs indicates pervasive low-temperature alteration (Grossman, 1980; MacPherson et al., 1988). Some of the alteration may have occurred long after formation. Numerous studies have reported disturbed isotopic systematics in CAIs and other components of carbonaceous chondrites (Gray et al., 1973; Tsumoto et al., 1976; Chen and Tilton, 1976; Chen and Wass-

erburg, 1981; Papanastassiou et al., 1987; Podosek et al., 1991; Bogdanovski and Jagoutz, 1999). The addition of the Re-Os decay system to the study of CAIs should provide additional constraints on the nature and timing of these processes.

2. SAMPLES

All samples, excepting sample F2 (obtained from L. Grossman, University of Chicago), were obtained from the Smithsonian Institution (sample numbers are the original USNM numbers; modifiers A, B, etc. represent different splits of the same inclusion). All CAIs are from the carbonaceous chondrite Allende (CV3), except for sample 3536-1, which is from the carbonaceous chondrite Leoville (CV3). Inclusions were selected on the basis of available petrographic, chemical, and isotopic data, and to represent the different groups of CAIs classified according to their rare earth element (REE) patterns. REE patterns in CAIs are often nearly unfractionated and flat (group V), sometimes with positive anomalies of Eu (group I), Eu and Yb (group VI), or showing negative anomalies of Eu and Yb in group III inclusions (Tanaka and Masuda, 1973; Grossman and Ganapathy, 1976; Grossman et al., 1977; Mason and Martin, 1977; Grossman, 1980; Mason and Taylor, 1982; MacPherson et al., 1988). The only types of CAIs showing strongly fractionated REE patterns are those with ca. 20× chondritic abundances of the light REE and decreasing abundances of the heavy REE (<1× chondritic for Lu) with a negative anomaly for Eu and a strong positive anomaly for Tm (group II). The REE patterns reflect volatility control with Eu and Yb being the most volatile REE, and Lu, Er, and Ho the most refractory REE (Boynton, 1975; Davis and Grossman, 1979). Two CAIs of this study are classified as group I, 7 CAIs group II, 2 CAIs group III, one CAI a group V, and another CAI a group VI (Table 1). Brief descriptions of the CAIs examined here follow.

Allende inclusions 3658 and 3898 are relatively coarse-grained melilite-rich inclusions with igneous textures (type A of Grossman, 1980) and were classified by Mason and Martin (1977) as group I inclusions. CAI 3898 is identical with inclusion D7 of Gray et al. (1973), a split of which yielded the initial $^{87}Sr/^{86}Sr$ of the solar system ("All"). Detailed petrographic descriptions, mineral chemical data, and Al-Mg and Rb-Sr isotopic data were given by Podosek et al. (1991). Both inclusions were split into subsamples (samples 3658-A, -B and 3898-A, -B in Table 1). Inclusion 3898 was also analyzed for W, Mo, and platinum group element (PGE) abundances by Fegley and Palme (1985).

Inclusions 3529-40, 3529-43, 3529-36.59, 4692, 3598, and "Dude" from Allende are fine-grained white- to variably pink-colored and show group II REE patterns. Fine-grained inclusions contain abundant spinel, melilite, and sometimes hibonite, as well as variable amounts of Ti-Al-rich clinopyroxene ("fassaite") and secondary phases (grossular, sodalite, nepheline). Petrographic descriptions and major and trace element data for CAIs 3529-40 and 3529-43 can be found in Mason and Taylor (1982). Detailed mineral chemical and Ti, U-Pb, and Mg isotopic data on CAI 3529-40, an inclusion that is very rich in hibonite, were reported by Niederer et al. (1981), Chen and Wasserburg (1981), and Davis and MacPherson (1988). Samples 4692 and 3598 were analyzed for major and trace element abundances (Mason and Martin, 1977). CAI 3529-36.59 consists of three fragments that are separated from each other by millimeter-size channels filled with Allende matrix. The inclusion was likely fragmented during accretion of the parent body. Inclusion Dude occurs in the chunk of Allende that contained CAI 3898, relatively close to fusion crust. On the basis of its fine-grained texture, pink color, and the low Re and Os contents (Table 1), we classified this inclusion as a group II CAI. CAI 3536-1 from the Leoville CV3 chondrite is another inclusion that shows a group II REE pattern (Mao et al., 1990). This inclusion is fine-grained, but compact and does not contain any secondary feldspathoids. It does, however, contain fractures, the surfaces of which are coated by Fe oxyhydroxides, most likely resulting from the oxidation of metal in Leoville during terrestrial alteration. For Re-Os analysis, fragments of the inclusion were selected that showed the least contamination by rust.

CAIs 3529-41 and 3529-42 represent inclusions with group III REE patterns. Inclusion 3529-41 (type B1) was split into three subsamples (A-C). Detailed petrographic, mineral chemical, major element, trace

element, and Sr and Mg isotopic data were reported previously (Lorin and Christophe-Michel-Levy, 1978; Mason and Taylor, 1982; Podosek et al., 1991). CAI 3529-42 is a composite inclusion (unaltered spinel-rich and altered spinel-poor domains) that was also analysed previously (Mason and Taylor, 1982; MacPherson et al., 1986; Mao et al., 1990).

Allende inclusion F2 is a large coarse-grained type-B2 inclusion (Grossman, 1980), which contains 40 vol. % melilite, 26% Mg-Al spinel, 27% fassaite, and 7% anorthite (S. B. Simon, personal communication, 1998). REE abundances suggest that inclusion F2 belongs to group V CAIs (unpublished data). A part of F2 was separated for the determination of major and trace element abundances by instrumental neutron activation analysis (INAA). After a long decay time different splits of F2 were analyzed for Re-Os isotopes. Subsamples 4 and 9 were split again (4A and B, and 9A and B, Table 1) and splits 4A and 9A were analyzed unspiked for Re and Os isotopic compositions. The other half of splits 4 and 9 (4B and 9B), and six other subsamples (2, 5A, 5B, 5C, 7, 1368, Table 1) of F2 were spiked with a mixed Re-Os spike (see below).

CAI 3529-Y is a melilite-rich group VI inclusion (Mason and Taylor, 1982) with a REE pattern complementary to group III CAIs.

3. ANALYTICAL TECHNIQUES

Fragments of inclusions were carefully separated from chunks of Allende using a steel needle. Some CAIs were obtained as crushed fragments and were separated with tweezers. Attached matrix or chondrule material was mechanically removed as much as possible. Samples prepared for digestions were estimated to be pure to 90 to 99%, with the remainder of the material being matrix that could not be removed. Most samples were ground to a fine powder in a small agate mortar (except samples F2-5A, -C, F2-4A, -B, F2-2, F2-9A, -B, which were digested without grinding).

Samples and a mixed ^{185}Re - ^{190}Os spike (Smoliar et al., 1996) were digested for 2 days at 240°C in reverse aqua regia (1–2 mL conc. HNO_3 + 0.5–1 mL conc. HCl) in sealed, small Pyrex glass tubes (“Carius tubes,” Shirey and Walker, 1995). This digestion procedure results in the decomposition, but not complete dissolution of silicates and oxides. After 2 days in the oven and multiple ultrasonic treatments, the CAI powder usually was converted into white dust-like or flocky powder. Osmium was separated from Re by solvent extraction into CCl_4 and back-extraction into HBr (Cohen and Waters, 1996). The Os fraction was further cleaned by microdistillation into HBr from a H_2SO_4 -dichromate solution (Roy-Barman, 1993). Rhenium was separated from the matrix by solvent extraction from dilute HNO_3 into a 1% solution of tribenzylamine in chloroform and back-extraction into NH_4OH (Walker, 1988). The Re fraction was purified on small columns loaded with AG1-X8 anion exchange resin using 0.8 mol/L and 5 mol/L HNO_3 .

The slush of residues and precipitates of six Carius tube digestions were subsequently dissolved via a miniaturized NaOH - Na_2O_2 fusion. The total dissolution technique will access any Re or Os that did not enter solution as a result of the Carius tube digestion. This alkaline fusion technique is also used to dissolve Os-Ir alloys and metallic Os and Ir spikes. before the fusion, CAI residues were washed five times in 2.5 mol/L HCl , to remove any dissolved Re and Os and dried. Spike was added before the samples were fused, assuming that residual Os and Re would be approximately 1% of the amount accessed during the Carius tube digestion. The fusion technique was described in detail previously (Morgan and Walker, 1989; Morgan et al., 1995). For the present purpose, the amounts of reagents were scaled down significantly. After fusion, Os was separated by distillation in H_2O_2 - H_2SO_4 , and collected in HBr or HCl -ethanol. Separation of Re from the pot liquid and cleanup of Os from the residues follow the techniques described above.

Rhenium and Os were measured by negative thermal ionization mass spectrometry (Creaser et al., 1991; Völkening et al., 1991) on the SECTOR 54 mass spectrometer at the University of Maryland using either faraday cups and static collection, or using the channeltron electron multiplier in pulse-counting mode (Table 1). Some CAI residues were run on a single collector NBS-designed mass spectrometer, on the faraday cup (3529-41C-r, 3898A-r) or on the electron multiplier (Dude-r, F2-7-r). Blank corrections were negligible for Os (0.4–1.5 pg), but the Re blank of 7 ± 5 pg ($n = 4$) comprised a significant

correction (<0.01–12.5%) in some samples processed by Carius tube digestion. Total chemistry blanks for alkaline fusion of CAI residues ranged between 0.8 and 1.4 pg for Os ($n = 2$) and 14 to 39 pg for Re ($n = 3$). The external precisions for $^{187}\text{Os}/^{188}\text{Os}$ of our Johnson-Matthey Os standard solution are $\pm 0.035\%$ (faraday cups) or 0.4% (electron multiplier). Errors on $^{187}\text{Re}/^{188}\text{Os}$ are $\pm 0.20\%$ or larger (Table 1), depending on the contribution and uncertainty of the Re blank.

4. RESULTS

4.1. General

The Re-Os isochron diagram in Figure 1 shows that most CAIs processed in Carius tubes (open symbols) plot on or close to the IIIA iron meteorite isochron (Smoliar et al., 1996). This is as expected if CAIs formed from a reservoir with a uniform Os isotopic composition during the first ~ 20 Ma of solar system evolution. A substantial number of samples, however, display significant offsets to the left or to the right of the iron meteorite isochron that are outside the errors imposed by analytical uncertainties of CAIs and the IIIA isochron (see next section). Details of the Re-Os systematics of splits of individual inclusions and between CAIs from the different groups as defined by their REE patterns are shown in $\Delta_{\text{Os}}-^{187}\text{Re}/^{188}\text{Os}$ diagrams in Figure 2. Δ_{Os} indicates the combined deviation of $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ of CAIs from the IIIA iron meteorite isochron:

$$\Delta_{\text{Os}} = 10^4 ({}^{187}\text{Os}/{}^{188}\text{Os}_{\text{CAI}} - 0.09524 + 0.07887 {}^{187}\text{Re}/{}^{188}\text{Os}_{\text{CAI}}) \quad (1)$$

${}^{187}\text{Os}/{}^{188}\text{Os}_{\text{CAI}}$ and ${}^{187}\text{Re}/{}^{188}\text{Os}_{\text{CAI}}$ are the measured values from the CAIs, whereas 0.09524 and 0.07887 are the initial ${}^{187}\text{Os}/{}^{188}\text{Os}$ and the slope of the IIIA iron meteorite isochron from Smoliar et al. (1996), respectively. Note that Δ_{Os} units reflect the deviation from the isochron in absolute values, multiplied by 10^4 . Smoliar et al. (1996) used the ε notation for the same equation to compute differences relative to their iron meteorite isochrons. Because the ε notation is commonly used for relative differences at the level of parts in 10,000, we adopt Δ as the more appropriate notation for differences between absolute values. (It should also be noted that the definition of Eqn. (1) in Smoliar et al. (1996) contains a typographical error in the caption of their Fig. 1.)

The ${}^{187}\text{Os}/{}^{188}\text{Os}$ and ${}^{187}\text{Re}/{}^{188}\text{Os}$ defined by CAIs processed in Carius tubes range to both higher and lower ratios than the ranges for the three major chondrite groups (Fig. 1). Fused residues (solid symbols in Fig. 1) of some CAIs extend the range in ${}^{187}\text{Os}/{}^{188}\text{Os}$ and ${}^{187}\text{Re}/{}^{188}\text{Os}$ even further towards lower values (Fig. 1). Bulk samples or splits of group II CAIs, on average, have higher ${}^{187}\text{Os}/{}^{188}\text{Os}$ and ${}^{187}\text{Re}/{}^{188}\text{Os}$ than any other group analyzed, and cover a much larger range in ${}^{187}\text{Os}/{}^{188}\text{Os}$ (0.12695–0.13770) and ${}^{187}\text{Re}/{}^{188}\text{Os}$ (0.409–0.535) than the other groups (Fig. 1). All group II CAIs with the exception of Dude (Fig. 2a,b), plot within uncertainties of the IIIA iron meteorite isochron. In part this may reflect the relatively large uncertainties for most group II samples, resulting from the lower quantities of Re and Os separated.

Bulk CAIs and splits of group I, III, V, and VI CAIs display a much more limited range in ${}^{187}\text{Os}/{}^{188}\text{Os}$ (0.1260–0.1272), similar to whole rock Allende (Fig. 2c) and the variations

Table 1. Rhenium and osmium isotopic data for calcium-aluminium-rich inclusions.^a

Sample	Group	Sample wt. (g)	Re (ppb)	Os (ppb)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	Δ _{Os}
3658A	I	0.0733	880.8	10,640	0.3987 ± 8	0.12654 ± 4	-1.5 ± 1.6
3658B	I	0.1284	538.2	6356	0.4079 ± 8	0.12667 ± 4	-7.4 ± 1.6
3658B-r	I	0.0425	73.27	1399	0.2523 ± 11	0.12637 ± 4	112.3 ± 1.6
3658B-t	I	0.1284	562.4	6820	0.3973 ± 8	0.12665 ± 4	0.8 ± 1.6
3898A	I	0.0705	426.7	5219	0.3939 ± 8	0.12621 ± 4	-0.9 ± 1.6
3898A-r	I	0.01597	66.00	1106	0.2873 ± 35	0.12135 ± 4	34.5 ± 3.1
3898A-t	I	0.0705	441.7	5469	0.3890 ± 8	0.12599 ± 4	0.7 ± 1.6
3898B	I	0.0250	427.4	5189	0.3968 ± 8	0.12664 ± 4	1.1 ± 1.6
3529-40	II	0.0984	65.67	680.2	0.4653 ± 8	0.13156 ± 5	-3.8 ± 1.7
3529-43	II	0.03424	8.19	75.7	0.5226 ± 91	0.13759 ± 17	11.3 ± 7.5
3529-36.59	II	0.0169	14.9	145	0.4960 ± 96	0.13393 ± 29	-4.2 ± 8.3
4692	II	0.0356	16.5	153.9	0.5178 ± 43	0.13600 ± 17	-0.8 ± 4.1
3598	II	0.00559	14.8	134	0.535 ± 30	0.13770 ± 14	2.6 ± 23.6
Dude	II	0.0565	20.0	226.3	0.4251 ± 28	0.12681 ± 4	-19.6 ± 2.7
Dude-r	II	0.01219	4.69	83.7	0.270 ± 61	0.1286 ± 4 ^b	121 ± 49
Dude-t	II	0.0565	21.0	244.3	0.4137 ± 41	0.12695 ± 21	-9.2 ± 4.1
3536-1 #	II	0.00645	8.7	103	0.409 ± 32	0.12716 ± 9	-3.2 ± 25.5
3529-41A	III	0.1200	598.8	7065	0.4083 ± 8	0.12717 ± 5	-2.7 ± 1.6
3529-41B	III	0.0627	323.1	41,240	0.3775 ± 8	0.12603 ± 4	10.2 ± 1.6
3529-41B-r	III	0.01796	128.6	2045	0.3029 ± 17	0.12413 ± 4	50.0 ± 1.9
3529-41B-t	III	0.0627	3268	41,820	0.3764 ± 8	0.12600 ± 4	10.7 ± 1.6
3529-41C	III	0.0598	695.9	8466	0.3960 ± 8	0.12658 ± 4	1.0 ± 1.6
3529-41C-r	III	0.01574	116.0	1688	0.3309 ± 24	0.12516 ± 4	38.2 ± 2.3
3529-41C-t	III	0.0598	726.4	8910	0.3928 ± 8	0.12651 ± 5	2.9 ± 1.6
3529-42	III	0.0440	629.1	7696	0.3938 ± 8	0.12645 ± 4	1.5 ± 1.6
F2-2	V	0.00094	527	6398	0.3966 ± 20	0.12680 ± 4	2.7 ± 2.2
F2-4A	V	0.00095				0.12659 ± 4	
F2-4B	V	0.00092	593	7314	0.3907 ± 18	0.12631 ± 9	2.5 ± 2.2
F2-5A	V	0.00034	1431	15,520	0.4443 ± 22	0.1264 ± 3	-38.8 ± 3.5
F2-5B	V	0.00016	604	7386	0.388 ± 10	0.1264 ± 2	5.9 ± 8.2
F2-5C	V	0.00075	417	5198	0.3861 ± 29	0.1269 ± 5	11.9 ± 5.7
F2-7	V	0.00046	287	3208	0.4308 ± 82	0.12639 ± 9	-28.3 ± 6.7
F2-7-r	V	0.00102	bl ^b	0.48 ^b		@	
F2-7-t	V	0.00046	287	3209			
F2-9A	V	0.00164				0.12654 ± 6	
F2-9B	V	0.00221	649.2	7908	0.3954 ± 8	0.12642 ± 4	-0.1 ± 1.6
F2-1368	V	0.00533	521.2	6420	0.3911 ± 8	0.12648 ± 4	3.9 ± 1.6
3529-Y	VI	0.01800	1563	19,040	0.3954 ± 8	0.12644 ± 4	0.1 ± 1.6

Abbreviations: bl: concentration at blank level; @: overspiked; Δ_{Os}: deviation of the sample from the IIIA iron meteorite isochron as defined in the text.

^a CAIs are from Allende, except #, which is from Leoville. Most data obtained by Carius tube digestion, except: r, residue from Carius tube digestion processed by Na₂O₂-NaOH fusion; t, calculated composition of combined residue and Carius tube data. Errors on ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os correspond to the last digits and reflect 2σ external precisions and uncertainties from the Re blank contribution.

^b Measured on the electron multiplier.

reported for other carbonaceous chondrites (Meisel et al., 1996; Walker et al., 2001). It should be noted that minor remnants of matrix and chondrule fragments attached to CAIs do not significantly affect the Re-Os data for group I, III, V, and VI CAIs. Osmium and Re abundances in matrix from Allende (ca. 680 ppb Os, Becker et al., 1999) are slightly lower than abundances in whole rock splits of Allende (750–780 ppb Os, Walker et al., unpublished data). Except for group II samples, most CAIs have much higher Os and Re contents (3200–42,000 ppb Os, Table 1) than matrix or chondrules (Becker et al., 1999).

Fine-grained group II inclusions have much lower Re and Os abundances (75.7–680.2 ppb Os) than other CAIs, and in some cases, the Re-Os systematics may be affected by minor amounts of matrix or chondrule fragments. Re-Os data for these chondrite components indicate that the ¹⁸⁷Os/¹⁸⁸Os of fine-grained Allende matrix (as low as 0.12096, Becker et al., 1999) is lower than the ¹⁸⁷Os/¹⁸⁸Os of Allende whole rocks (0.12610–0.12643, Meisel et al., 1996; Walker et al., unpub-

lished data), and chondrules and coarse metal (0.1273–0.1305, Becker et al., 1999). Compared to these components, many group II CAIs show more radiogenic ¹⁸⁷Os/¹⁸⁸Os (Fig. 1). The group II CAIs 3529-40, 4692, and Dude are more than 99% pure. Mass balance calculations show that the effects of admixed chondrite matrix or chondrules are negligible for these inclusions. However, calculations also indicate that the measured ¹⁸⁷Os/¹⁸⁸Os of those group II CAIs that have an estimated 5 wt. % matrix or chondrules attached (3529-43, 3529-36.59, 3598, and 3536-1) may be biased to ratios of 2 to 10% less than the pure CAI. Because of the difficulty of precise estimation of the mass fraction and composition of attached matrix or chondrule fragments, no correction of the measured Re-Os data of these less pure inclusions was attempted. Regardless of the effects of minor matrix or chondrules, CAIs with group II REE patterns show mostly elevated Re/Os and radiogenic ¹⁸⁷Os/¹⁸⁸Os, very distinct from other groups of CAIs.

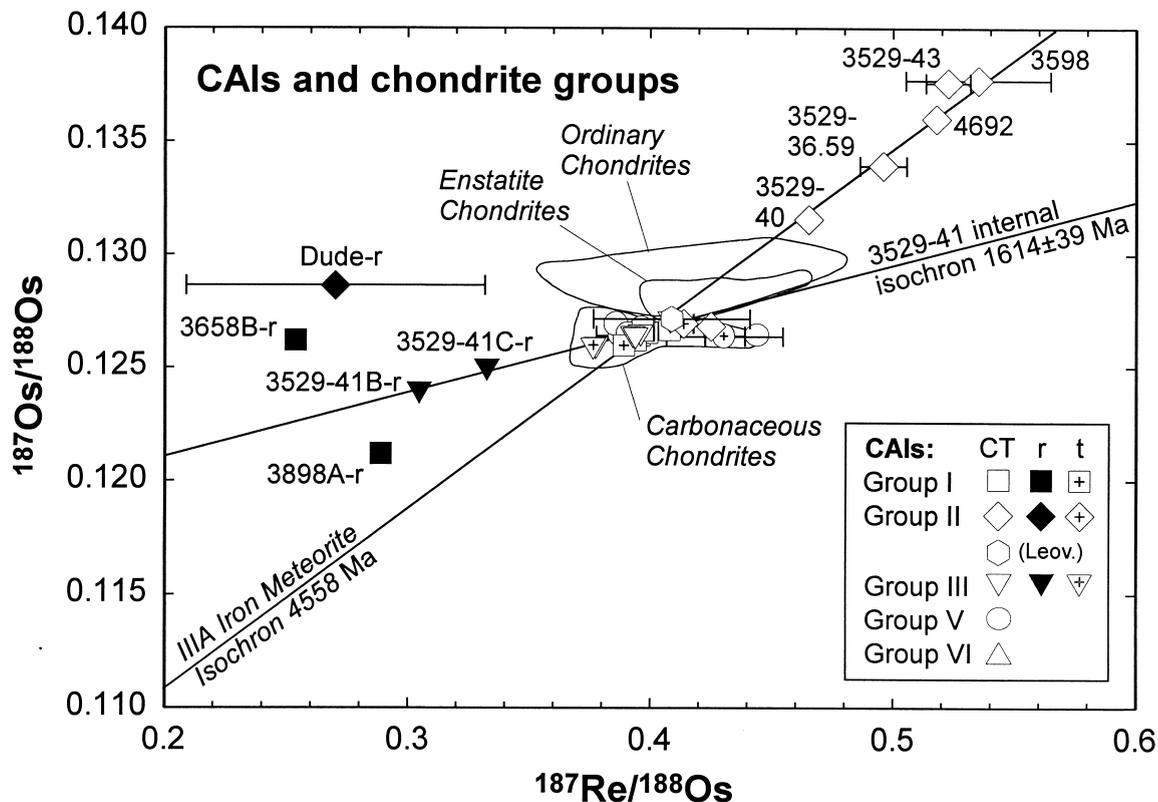


Fig. 1. Re-Os isochron diagram. Data are from Table 1. Error bars are shown or are smaller than the size of symbols. CT: Carius tube digestions. r: CAI “residues” from Carius tube digestions. These residues were processed using a Na_2O_2 -NaOH fusion technique. t: combined residue and Carius tube data. The different groups of CAIs are distinguished on the basis of their REE patterns. Sample numbers for CAIs that show group II REE patterns and CAI residues are shown. Sample numbers of other inclusions are indicated in Fig. 2. Fields defined by carbonaceous, enstatite, and ordinary chondrite bulk rock data (Meisel et al., 1996; Chen et al., 1998; Walker et al., 2001) are outlined. Only chondrite data obtained by high-temperature closed-system digestion in Carius tubes were used. The IIIA iron meteorite reference isochron is from Smoliar et al. (1996). Also shown is a five-point internal errorchron obtained on Carius tube fractions and residues of CAI 3529-41 (details see Fig. 2). Analytical uncertainties in Figs. 1 and 2 are at the 2σ level.

4.2. Small-scale Isotopic Variability of the Carius Tube Data

Results shown in Fig. 2 indicate that of the 24 samples for which Re-Os data were obtained by the Carius tube technique, 16 samples plot within analytical uncertainties of the IIIA isochron ($\pm 1.9 \Delta_{\text{Os}}$ units), 3 samples plot within $\pm 5 \Delta_{\text{Os}}$ units (3529-43, F2-5C, F2-1368) from the IIIA isochron, and 5 samples show larger positive (3529-41B) or negative deviations (F2-5A, F2-7, Dude, 3658B).

CAIs with group I, III, V, and VI REE patterns processed by Carius tube digestion show a limited variability of ca. 0.9% in $^{187}\text{Os}/^{188}\text{Os}$ (0.12603–0.12717) between different inclusions and for different splits of the same inclusion. The three splits of 3529-41 processed by Carius tube digestion define a linear array with a shallower slope than the IIIA isochron (Figs. 1, 2, see next section). The split with the lowest $^{187}\text{Os}/^{188}\text{Os}$ (3529-41-B, Table 1) has unusually high Re and Os abundances (3231 and 41,240 ppb, respectively).

Six splits (2, 4B, 5B, 5C, 9B, 1368) of inclusion F2 (group V) show variations in $^{187}\text{Os}/^{188}\text{Os}$ of as much as 0.5%, however, they cluster relatively close to the IIIA isochron (Fig. 2b). These small-scale variations ($\Delta_{\text{Os}} = -0.1 \pm 1.6$ to 11.9 ± 5.7)

are not correlated with Re/Os, which shows a total variation of less than 3% (Table 1). In contrast, splits F2-5A and F2-7 plot -38.8 and -28.3Δ units below the iron meteorite isochron (Fig. 2b). Of note, split 5A is characterized by relatively high Re and Os abundances (1431 and 15,520 ppb, respectively).

Two unspiked splits of inclusion F2 (F2-4A and F2-9A) were analyzed for their Re and Os isotopic composition to search for resolvable anomalies in the abundances of the stable isotopes of Re and Os. The $^{185}\text{Re}/^{187}\text{Re}$ of these samples (0.5985 ± 12 and 0.5976 ± 2 , respectively) agree with the value for our Re standard (0.5984) within the external mass spectrometric precision of $\pm 0.13\%$. The Johnson-Matthey Os standard solution that was used to monitor long-term reproducibility yields fractionation-corrected $^{186}\text{Os}/^{188}\text{Os} = 0.119847 \pm 25$, $^{189}\text{Os}/^{188}\text{Os} = 1.21967 \pm 16$, and $^{190}\text{Os}/^{188}\text{Os} = 1.9834 \pm 5$ (errors refer to the last digits and are 2σ external precisions). Fractionation-corrected $^{190}\text{Os}/^{188}\text{Os}$ (F2-4A: 1.98315 ± 6 , F2-9A: 1.98337 ± 12) and $^{189}\text{Os}/^{188}\text{Os}$ (F2-4A: 1.21956 ± 6 , F2-9A: 1.21971 ± 11) of unspiked samples agree with the Os standard at the 0.03 and 0.01% level, respectively. The fractionation-corrected $^{186}\text{Os}/^{188}\text{Os}$ of unspiked samples (F2-4A: 0.11981 ± 3 , F2-9A: 0.11988 ± 7) and standard agree

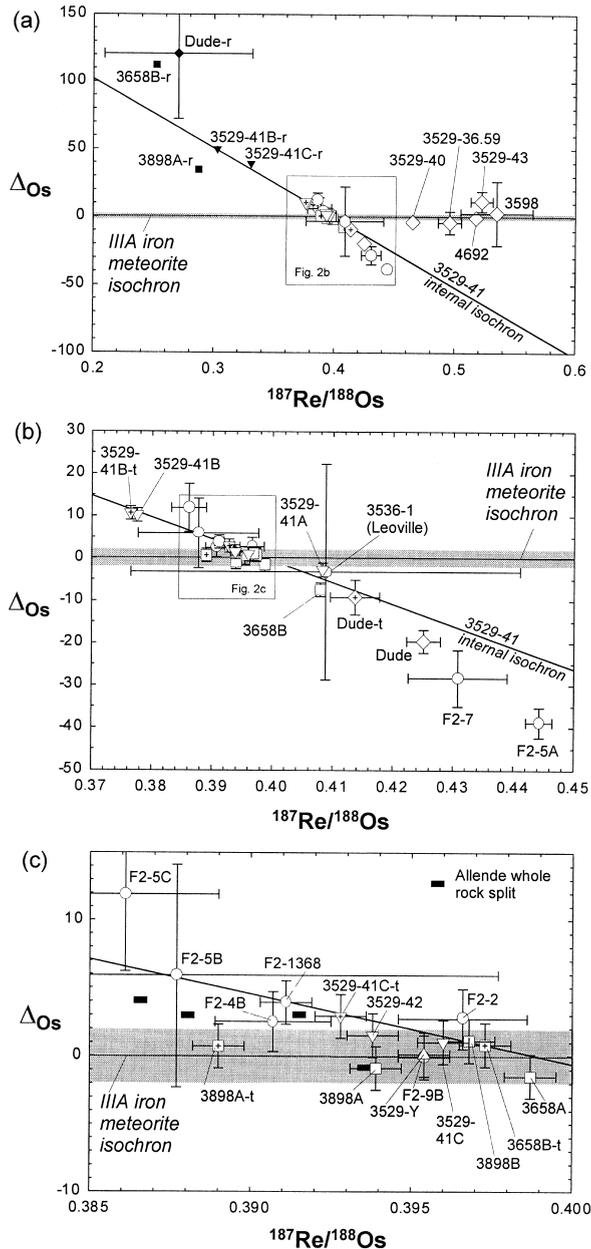


Fig. 2. (a–c) Δ_{Os} vs. $^{187}Re/^{188}Os$ diagrams. Δ_{Os} reflects the absolute deviation of a sample from the IIIA iron meteorite isochron (Smoliar et al., 1996). The IIIA isochron is shown as a horizontal line at $\Delta_{Os} = 0$ and the gray band reflects the 2σ uncertainty of the isochron in Δ_{Os} units. Also shown is the 1614 Ma internal isochron of CAI 3529-41. Analytical uncertainties of Allende whole rock splits are shown in (c) and are similar to the smallest error bars of CAIs in (c).

within 0.03 to 0.06%. A comparison of unspiked and spiked splits of subsamples 4 and 9 shows minor differences in $^{187}Os/^{188}Os$ between 4A and 4B of 0.2%, and between 9A and 9B of 0.05%, respectively (Table 1).

Inclusion 3529-Y was the only group VI CAI analyzed. It has relatively high Re and Os abundances (1563 and 19,040 ppb, respectively) and plots within analytical uncertainties of the IIIA reference isochron and most group I inclusions (Fig. 2c).

4.3. CAI Residues and Combined Residue and Carius Tube Data

Carius tube digestions of silicates and oxides usually leave cloudy solutions consisting mostly of precipitates from the high-temperature digestion, such as silica from the sample and glass tube and other compounds. Here these precipitates will be referred to as “residues” of the Carius tube digestion. To access Re and Os in potentially undigested phases, residues (-r in Table 1) from six CAI splits processed in Carius tubes were digested by Na_2O_2 -NaOH fusion (see “Analytical Techniques” for details). This technique results in complete dissolution of residues, albeit at the cost of higher Re blanks than for Carius tube digestions. Samples were selected that show variable deviations from the IIIA isochron for their Carius tube data. Table 1 also shows the calculated Re and Os abundances, and $^{187}Re/^{188}Os$, $^{187}Os/^{188}Os$, and Δ_{Os} values for Carius tube data and residue data combined (-t in Table 1).

The amount of Os in the analyzed residues ranges between 0.03% (F2-7-r) and 7.39% (Dude-r) of the total amount of Os in residue and Carius tube data combined. Slightly lower equivalent percentages of Re were found in the residues. $^{187}Os/^{188}Os$ in the residues show a large range from 0.12135 (3898A-r) to 0.1286 (Dude-r). The measured $^{187}Re/^{188}Os$ of all analyzed residues are substantially lower than in the corresponding Carius tube fractions, leading to large positive Δ_{Os} for the residues (Figs. 1, 2a, Table 1). The residue of the group II inclusion Dude has a higher $^{187}Os/^{188}Os$ (0.1286) than the Carius tube fraction (0.1268). This is opposite to what is observed in other CAI groups where residues have similar or lower $^{187}Os/^{188}Os$ than corresponding Carius tube fractions. Unfortunately, because of the low Re content of Dude-r, the uncertainty on $^{187}Re/^{188}Os$ is large (Table 1). The deviation of the combined inclusion from the IIIA isochron is less than for the Carius tube fraction ($\Delta_{Os} = -9.2 \pm 4.1$ vs. $\Delta_{Os} = -19.6 \pm 2.7$, respectively).

For sample 3658B, the calculated $^{187}Os/^{188}Os$ of the combined residue and Carius tube fraction is indistinguishable from the Carius tube fraction. The low $^{187}Re/^{188}Os$ in the residue of this sample, however, results in a shift of Δ_{Os} from -7.4 in the Carius tube fraction to 0.8 in the combined residue and Carius tube data. In 3898A, residue and Carius tube fraction have very different $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ (Table 1, Figs. 1, 2). The change in Δ_{Os} from Carius tube data (3898A, $\Delta_{Os} = -0.9$) to combined CAI split (3898A-t, $\Delta_{Os} = 0.7$) is minor, and within uncertainties of the IIIA iron meteorite isochron. The amount of Re and Os in F2-7-r was within the blank range (Re) or slightly above (Os), hence, the combined inclusion (F2-7-t) is little different from the Carius tube result.

Residues 3529-41B-r and 3529-41C-r show significantly lower $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ than their corresponding Carius tube fractions (Figs. 1, 2). These residues contain little Re and Os relative to the bulk inclusion splits (1.40% and 4.99% of the Os, respectively). Consequently, the position of combined Carius tube and residue data show only minor shifts in the isochron diagram, relative to the Carius tube data (Fig. 2b,c). It should be noted that the combined inclusion splits 3529-41B-t and 3529-41C-t plot further from the IIIA reference isochron than the Carius tube fractions. In conjunction with the Carius tube data (3529-41A, B, C), residues 3529-41B-r and

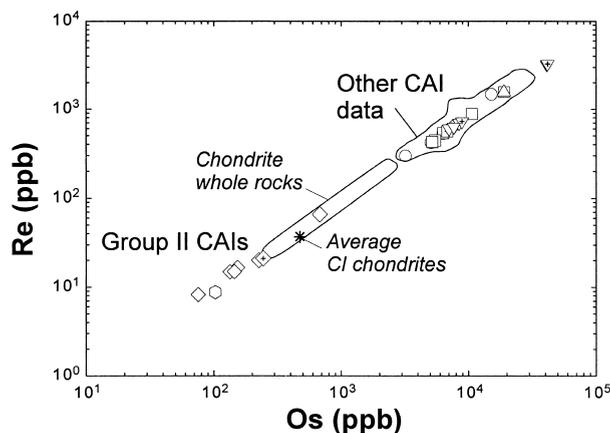


Fig. 3. Re and Os abundances in bulk CAIs and CAI splits. High-precision data from this study (Carius tube data or combined Carius tube and residue data; symbols as in previous figures) and sample Big Al-4 (Chen et al., 1999). CAI data of lower precision plot in the field shown in outline (Palme and Wlotzka, 1976; Mason and Taylor, 1982; Palme et al., 1994). The field for chondrite bulk rocks is based on recent high-precision data (Jochum, 1996; Meisel et al., 1996; Chen et al., 1998; Walker et al., 2001; and unpublished data). Average CI chondrites from Anders and Grevesse (1989).

3529-41C-r define a linear array that, if interpreted as having age significance, yields an age of 1614 ± 39 Ma ($^{187}\text{Os}/^{188}\text{Os}_i = 0.11588 \pm 25$, MSWD = 43.4).

4.4. Re and Os Abundance Variations

The Re and Os abundances of CAIs analyzed in this study are similar to the range defined by abundance data from the literature (Fig. 3). Except for the less abundant type II inclusions, most CAIs have, on average, about one order of magnitude higher concentrations of Re and Os than whole rock carbonaceous chondrites (Jochum, 1996; Walker et al., 2001; Wasson and Kallemeyn, 1988), or chondrite components such as matrix, coarse-grained metal and chondrules (Becker et al., 1999). Although all groups of CAIs show large variations in Re and Os abundances, there is no overlap between the abundance data of group II CAIs and the other groups. Group II inclusions are characterized by one to two orders of magnitude lower Re and Os abundances compared to other CAIs (Table 1, Fig. 3), in agreement with less precise Os abundance data published previously (Mason and Taylor, 1982). The variability of Re and Os abundances in group II CAIs comprises one order of magnitude (75.7–680.2 ppb Os), whereas the variability of the other groups together is somewhat larger (3209–41,820 ppb Os).

5. DISCUSSION

5.1. Why Do Some CAIs Plot on the Iron Meteorite Reference Isochron and Others Do Not?

It is shown in Figure 1 that early established differences in Re/Os are the major cause of the observed variability of $^{187}\text{Os}/^{188}\text{Os}$ in CAIs from carbonaceous chondrites. In this section, the origins of the small, but significant deviations of some

samples from the IIIA iron meteorite isochron are discussed. Several possible scenarios are considered.

5.1.1. Early Solar System Processes

Deviations of some CAIs from the IIIA reference isochron could reflect either chemical differentiation processes in the early solar nebula or primordial heterogeneities in $^{187}\text{Os}/^{188}\text{Os}$. Both options are very unlikely for these samples.

Volatility-controlled chemical differentiation processes such as condensation or evaporation would have to cause extreme fractionations of Re/Os and effective isolation of nonsolar Re/Os components from the solar gas over periods of hundreds of thousands or several million years. Then, another fractionation would be necessary to reverse the increased Re/Os back to the near-chondritic values observed. No primitive solar system objects with sufficiently high Re/Os have, as yet, been identified. No other evidence exists that such fractionations occurred. Primordial heterogeneities in $^{187}\text{Os}/^{188}\text{Os}$ should likely be accompanied by a “nonsolar” mix of stable isotopes of other isotopes of Os. None of the CAI samples that plot off the IIIA isochron show resolvable anomalies in other Os isotopic ratios.

5.1.2. Analytical Issues

There are at least two types of analytical issues that could lead to nonisochronous behavior of CAIs: (1) random blank problems, and (2) incomplete dissolution of some phases with concurrent preferential leaching of Re or Os. The only significant blank problem to be considered is the possibility of underestimating or overestimating the Re blanks. Osmium blanks were negligible for this suite of samples. Randomly high Re blanks may be invoked for two samples where sample sizes are small and the total amount of Re analysed was low (F2-5A, F2-7, Fig. 2b, Table 1). For F2-7, a Re blank correction of 18 pg, instead of 7 pg, would move this sample within error of the IIIA isochron. However, a high Re blank of 60 pg would have to be assumed, in order for sample F2-5A to plot on the IIIA isochron. Such high blanks were never observed using the analytical procedures outlined previously. Three of the nonisochronous samples contain sufficiently large quantities of Re that blanks were negligible. Of these, sample 3529-41B (204.9 ng Re) plots to the left (Fig. 2a, Table 1), and samples 3658-B (72.21 ng Re) and 3529-41A (71.86 ng Re) plot to the right of the IIIA isochron (Fig. 2a). Thus, nonisochronous behavior in most instances is probably not the result of inadequate blank corrections.

Another possibility for the small-scale deviations about the isochron is incomplete dissolution of Re- and Os-bearing phases, with concurrent selective removal of Re relative to Os or vice versa. Petrological studies of CAIs have identified a plethora of sulfides and alloys (“Fremdlinge”) that host variable amounts of Re, Os, and other siderophile elements (El Goresy et al., 1978; Armstrong et al., 1987; Blum et al., 1989; Sylvester et al., 1990). Detailed work by Palme et al. (1994) has shown that a large fraction of the budget of the HSE in CAIs resides in submicron-size alloy inclusions contained in silicates and oxides. The high-temperature closed-system digestion procedure employed here is probably the most effective and reli-

able one available for the equilibration of spike solutions and samples, given the need to minimize Re and Os blank contributions (Shirey and Walker, 1995; Smoliar et al., 1996; Shen et al., 1996). It should be noted, however, that refractory HSE alloys, particularly Ir-Os alloys, may be difficult to dissolve in acids. This problem may become worse if alloys are mantled by silicates or oxides.

Preferential dissolution of Re- or Os-rich phases alone would result in correlated shifts of Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ along the IIIA isochron, and hence, not account for nonisochronous behavior. Preferred leaching of Re relative to Os during sample digestion is required by those samples that plot to the right of the IIIA isochron, whereas the opposite would have to occur in the case of samples that plot to the left of the IIIA isochron. One of the intricacies of this explanation is that the radiogenic ^{187}Os that resided in Re-rich phases or domains must be retained or redeposited electrochemically without equilibrating with the spike solution. Apparent electrochemical redeposition of Re and Os has been previously observed while acid leaching iron meteorites at low temperatures (Morgan et al., 1995; Smoliar et al., 1996). It has not been, however, demonstrated to occur during Carius tube digestions at high temperatures. Although such chemical fractionations cannot be ruled out, it is difficult to conceive that radiogenic Os leached with Re can escape equilibration with the enriched isotopic Os tracer in aqua regia at the high-temperature and closed-system conditions of Carius tube digestions. More importantly, the errorchron relationship obtained for Carius tube data and residues of splits of CAI 3529-41 is difficult to explain by either blank or digestion problems, and suggests that some of the small-scale deviations result from other processes.

5.1.3. Late-stage Open System Behavior

The most plausible explanation for some or all of the samples that deviate from the IIIA isochron is late-stage movement of Re or Os in the CAI samples, either during terrestrial alteration or during alteration on the parent body. The most clear-cut evidence for a late disturbance of the Re-Os system comes from CAI sample 3529-41 that yields an apparent internal errorchron age of 1614 ± 39 Ma defined by three splits processed in Carius tubes and two of the residues (Figs. 1, 2; Table 1). We emphasize again that this alkaline fusion technique results in complete dissolution of any remaining Re and Os in the residues. It is inconceivable that such a linear correlation could be produced by blank problems because the amounts of Re and Os in these splits were high (Table 1). Preferred leaching is also a problematic explanation, particularly, because the residues of the Carius tube digestions were processed in a different way, yet are part of the correlation. Late open-system behavior of CAIs from Allende has been noted previously from disturbed systematics of other radioactive decay systems. Gray et al. (1973), Tatsumoto et al. (1976), and Podosek et al. (1991) found evidence for disturbed Rb-Sr systematics in CAI splits from Allende and in other components of this meteorite. U-Pb studies of CAIs and matrix from Allende indicate a late (<300 Ma) disturbance of the U-Pb system (Chen and Tilton, 1976; Chen and Wasserburg, 1981; Tatsumoto et al., 1976). Results on CAI splits and leach fractions of CAIs from Allende indicate that even the relatively

robust Sm-Nd system shows evidence for relatively late mobility, presumably caused by some type of aqueous alteration (Bogdanovski and Jagoutz, 1999; Papanastassiou et al., 1987). Because of the variable mobility of Re and Os during aqueous alteration (Xiong and Wood, 1999), similar processes may have affected the Re-Os systematics of the CAIs, and likely the Re-Os systematics of some chondrite whole rocks (Walker et al., 2001, and unpublished data). The secondary isochron age of 1614 Ma for inclusion 3529-41 strongly suggests that, at least for this CAI, the alteration event that disturbed the Re-Os systematics occurred in an asteroidal environment.

We conclude that sample splits that form a secondary isochron clearly require relatively late-stage open-system behavior. Although it cannot be excluded that preferred leaching of Re and redeposition of radiogenic Os may be responsible for some small-scale deviations from the IIIA iron meteorite isochron, such a scenario is difficult to conceive during a high-temperature Carius tube digestion. Because most group II CAIs plot on the IIIA isochron, their high Re/Os must be the result of processes that occurred in the early solar system.

5.2. Multiple Components in CAIs

Davis and Grossman (1979) pointed out that the REE patterns of group II CAIs are best explained by the presence of two components in these inclusions, one component with a strongly fractionated REE pattern, and a second component with a nearly unfractionated REE pattern. The presence of two distinct components in CAIs is also indicated by the hyperbolic distribution of a large number of CAI samples in a La/Yb-Eu/Eu* diagram (Fig. 3 in Mason and Taylor, 1982). Although not all CAIs examined here are isochronous, the deviations are on the order of a few percent at most. Consequently, this work comprises the most precise set of Re and Os abundance data currently available for CAIs, and the abundances of Re and Os can also be examined with respect to multicomponent mixing. A correlated data distribution in the $^{187}\text{Os}/^{188}\text{Os}$ -Os diagram, with $^{187}\text{Os}/^{188}\text{Os}$ as the preferred proxy for Re/Os (see caption of Fig. 4) supports the contention that at least two components are necessary to explain the Re-Os systematics in CAIs. The two endmembers are most closely approximated by extreme group II samples (La/Yb > 30, Eu/Eu* = 0.1–0.2, $^{187}\text{Os}/^{188}\text{Os}$ > 0.138, Re/Os > 0.11, low HSE contents), and group I samples (La/Yb = 1–2, Eu/Eu* > 1.5–1.6, $^{187}\text{Os}/^{188}\text{Os}$ = 0.1264–0.1265, Re/Os = 0.081–0.083, high HSE contents). Mason and Taylor (1982) showed that group III and V CAIs lie between group II and I inclusions. Some group III CAIs (e.g., 4698 and 3593 in Mason and Martin, 1977) show clear affinities to group II CAIs (high La/Yb, low Eu/Eu*, low abundances of refractory lithophile elements). The data distribution in the $^{187}\text{Os}/^{188}\text{Os}$ -1/Os diagram (inset, Fig. 4) shows that at least one other component with low Os and slightly elevated Re/Os is required to explain the offset of group II samples Dude (Allende) and 3536-1 (Leoville) from the correlation defined by the remaining group II samples.

5.3. Possible Origins of Differences between Group II and Other CAIs

At least two different classes of models can explain the high Re/Os in group II CAIs. In one class of models, the Re-Os

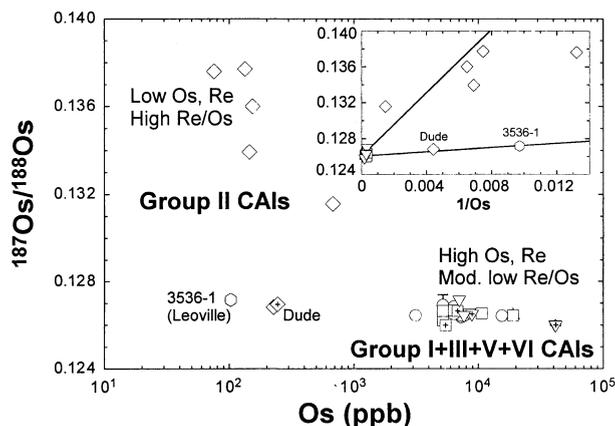


Fig. 4. $^{187}\text{Os}/^{188}\text{Os}$ vs. Os (in ppb) diagram. $^{187}\text{Os}/^{188}\text{Os}$ is used as a precise proxy for Re/Os because some CAIs have a Re/Os that is too high or too low for their $^{187}\text{Os}/^{188}\text{Os}$. The correlation suggests that group II CAIs, and possibly other CAI groups as well, contain at least two distinct components, a high-Re/Os, low-Os-Re component and a low-Re/Os, high-Os-Re component. Samples Dude from Allende and 3536-1 from Leoville plot off the main trend and require a different Re/Os in the high-Re/Os endmember compared to other group II samples. The inset shows the data on a $^{187}\text{Os}/^{188}\text{Os}$ vs. $1/\text{Os}$ diagram, in which binary mixtures form straight lines. The lines delimit mixing between the low-Re/Os component and high-Re/Os components. Symbols as in previous figures.

fractionation occurred as a consequence of multiple condensation events at very high temperatures. In a second class of models, the high Re/Os component reflects moderate- to low-temperature alteration under oxidizing conditions.

5.3.1. Re-Os Fractionation during Condensation at High Temperatures

At the very reducing conditions in a gas of solar composition, the highly refractory nature of Re and Os and their similar 50% condensation temperatures limit significant fractionation of Re/Os to a relatively narrow temperature interval (Fegley and Palme, 1985; Grossman, 1973; Palme and Wlotzka, 1976; Sylvester et al., 1990). This may change, however, at higher $f\text{O}_2$ at which Re is more volatile than Os (Palme et al., 1998), and may be preferentially retained in the gas phase relative to Os during condensation of refractory metal alloys. This model is one of several possible explanations for the origin of W and Mo depletions, relative to refractory PGE in refractory metal nuggets from CAIs and some bulk CAIs (Fegley and Palme, 1985; Sylvester et al., 1990; Palme et al., 1994). Tungsten and Mo form volatile oxides at lower $f\text{O}_2$ than Re and Os (Fegley and Palme, 1985; Palme et al., 1998), and may display depletions, even if Re and Os are unfractionated. The interpretations of these data in terms of high- $f\text{O}_2$ condensation models are not unequivocal. Alternative explanations such as parent body alteration (Wasson and Krot, 1994) or very localized high- $f\text{O}_2$ environments near evaporating dust clumps (Krot et al., 1993) are favored by others. Another trade-off for condensation models at variable $f\text{O}_2$ may be the expected correlated behavior of some lithophile elements that are moderately refractory under reducing conditions, but should be highly volatile at higher $f\text{O}_2$ (e.g., Ce^{4+} , Boynton, 1978). CAIs and ultrarefractory inclu-

sions sometimes show Ce anomalies; however, the behavior of Ce appears to be erratic. Many group II inclusions have no Ce anomalies, while some do (Mason and Martin, 1977; Mason and Taylor, 1982; Mao et al., 1990; Sylvester et al., 1992).

5.3.2. Re-Os Fractionation during Low-temperature Alteration in the Early Solar System

Evidence for secondary alteration processes is common in many primitive solar system objects (Zolensky and McSween, 1988). Alteration of dust particles may have occurred very early by interaction of grains with cooling solar gas at moderate to low temperatures (Bischoff and Palme, 1987). Alteration of millimeter to centimeter-size objects, such as CAIs and chondrules that originally underwent one or more high-temperature stages, is also documented (MacPherson et al., 1988; Zolensky and McSween, 1988). Finally, low-temperature alteration processes occurred on the parent bodies of chondritic meteorites (Krot et al., 1995). Isotopic studies have shown that some alteration processes on parent bodies occurred within the first 15 to 20 m.y. after the formation of the solar system (Endress et al., 1996; Hutcheon et al., 1998).

Most CAIs show alteration in the form of secondary phases such as anorthite, grossular-rich garnet, nepheline, sodalite, and a number of less abundant silicates (MacPherson et al., 1988). Moderate to low-temperature alteration of CAIs is characterized by the introduction of water, sulfur, and other volatile elements and compounds, and an environment of higher $f\text{O}_2$ than that assumed for the early high-temperature evolution of the solar nebula (Armstrong et al., 1987; Bischoff and Palme, 1987; Blum et al., 1989; Palme et al., 1994). Fremdlinge show abundant secondary sulfides, alloys, oxides, phosphates, and phases such as scheelite and powellite that indicate oxidation and mobilization of W and Mo (El Goresy et al., 1978; Armstrong et al., 1987; Bischoff and Palme, 1987; Blum et al., 1989; Palme et al., 1994).

Alteration of group II CAIs could provide a compelling explanation for the high Re/Os and the much larger variability of Re/Os in these samples. If the variable and generally high Re/Os in group II CAIs reflect low-temperature alteration, it must have occurred very early, because of the correlated $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 1). Two scenarios are conceivable.

In the first scenario, component 2 that introduced refractory lithophile and volatile elements in group II CAIs may have been characterized by suprachondritic ratios of volatile to refractory elements (e.g., high Re/Os) acquired during alteration of chondritic precursor dust under oxidizing conditions. However, this explanation is very unlikely, because it would result in preferential evaporative loss of Re over Os (Palme et al., 1998), the opposite of what is observed.

In a second scenario, component 1 in group II CAIs may represent a condensate from a gas that lost its inventory of highly refractory elements in a previous condensation episode without significant fractionation of Re and Os relative to solar composition. Small amounts of Re, Os, and other refractory and volatile elements in group II CAIs were then added in chondritic relative proportions in the form of component 2 (Davis and Grossman, 1979). High Re/Os were acquired during a later stage by low-temperature alteration of the assembled CAIs, either in a nebular environment, or, more likely, on the parent

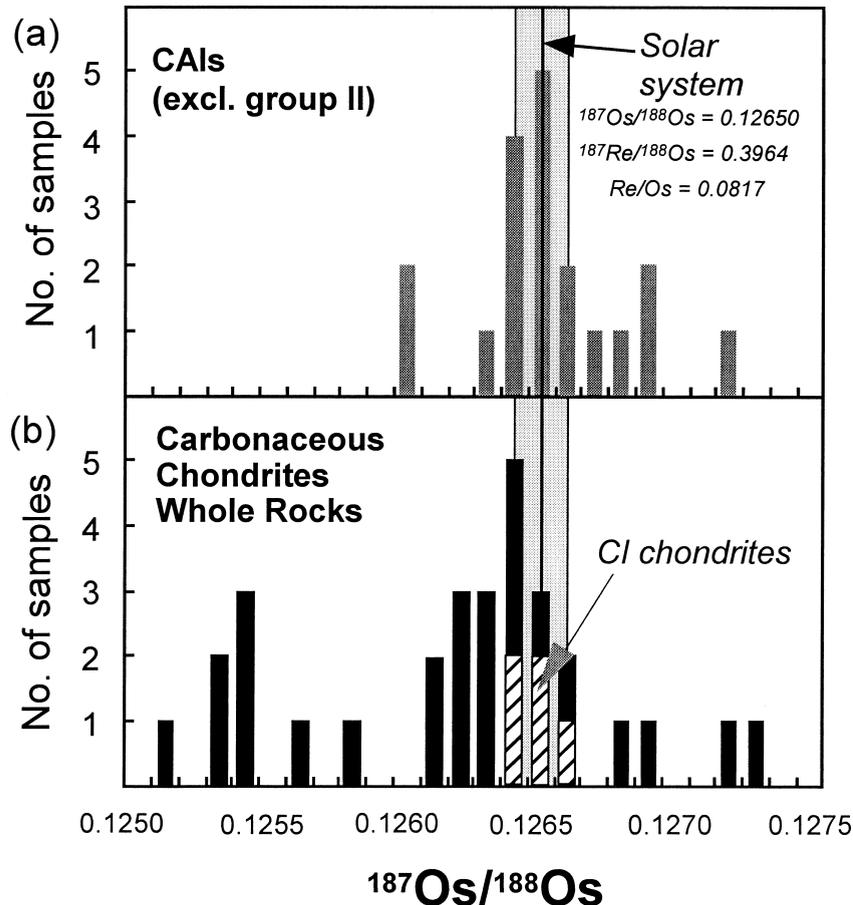


Fig. 5. Histograms for $^{187}\text{Os}/^{188}\text{Os}$ in group I, III, V, and VI CAIs (a), and carbonaceous chondrite whole rocks (b). CAI data include sample Big Al-4 (Chen et al., 1999), but exclude data for group II inclusions from the present study. The carbonaceous chondrite whole rock data comprise only data obtained by high-temperature closed-system digestion in Carius tubes (Meisel et al., 1996; Walker et al., 2001; and unpublished data). $^{187}\text{Os}/^{188}\text{Os}$ of CAIs with relatively unfractionated REE patterns (groups I, III, V, and VI) overlap with $^{187}\text{Os}/^{188}\text{Os}$ for CI chondrites (b), suggesting that the mean of the CAI distribution at 0.12650 ± 28 represents a precise estimate for the modern $^{187}\text{Os}/^{188}\text{Os}$ of the solar system. Assuming an age similar to IIIA iron meteorites yields a value of 0.3964 for the modern $^{187}\text{Re}/^{188}\text{Os}$ of the solar system.

body (Wasson and Krot, 1994). Palme et al. (1994), in a detailed study of altered CAI fragments and Fremdlinge, have shown that oxidation of W and Mo likely occurred while the CAI was already assembled, because the W and Mo depletions in some CAI fragments are balanced by the W and Mo abundances in others due to the presence of scheelite and powellite in the latter. This suggests millimeter-scale mobility of W and Mo during alteration of CAIs. Sulfide- and metal-bearing veins and fractures associated with CAIs from Allende indicate the possibility of Re and Os mobility during alteration (Campbell et al., 1999). For group II CAIs, medium to low-temperature alteration appears to be a feasible alternative to condensation at high $f\text{O}_2$ because the Re and Os abundances in these inclusions are commonly one order of magnitude lower than in bulk chondrites (Fig. 3). This process requires either the addition of Re from external sources, potentially the chondrite host, loss of Os, or both.

The high-precision $^{187}\text{Os}/^{188}\text{Os}$ database for group I, III, V, and VI CAIs suggests very limited fractionation of Re/Os on

the scale of bulk inclusions, or millimeter-size inclusion splits (Figs. 1, 5a). It is noteworthy that the results from the CAI residues indicate that some CAIs contain minor components that are not only difficult to digest, but also show significantly lower $^{187}\text{Os}/^{188}\text{Os}$ than bulk inclusions (Fig. 1). These observations contrast with the large variability in Re and Os abundances observed in bulk or split analyses of such inclusions (Figs. 3, 4, Table 1, see also Fegley and Palme, 1985; Bischoff and Palme, 1987; Palme et al., 1994). The variability in Re and Os (and other PGE) abundances may reflect (1) heterogeneous accumulation of alloy particles, (2) secondary mobilization during melting, or (3) low-temperature alteration of the inclusion 4.5 Ga ago (Blum et al., 1989). The narrow range in Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 5a) in these inclusions, and the similarity of the data with Re-Os data obtained on bulk carbonaceous chondrites (Fig. 5b; Walker et al., 2001), indicate that melting and low-temperature alteration in the early solar system did not significantly affect Re/Os in group I, III, V, and VI CAIs on the scale of a bulk inclusion or inclusion split.

5.4. Modern $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ of the Bulk Solar System

High-precision Re–Os abundance and isotopic data on carbonaceous chondrite whole rocks (Meisel et al., 1996; Walker et al., 2001, and unpublished data) in conjunction with $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ of CAIs that show unfractionated or nearly unfractionated REE patterns (groups I, III, V, and VI) may be used to precisely constrain the modern $^{187}\text{Os}/^{188}\text{Os}$ of the solar system. Group II CAIs are excluded because they are volumetrically minor and their refractory lithophile and siderophile element compositions are unlike those of most other known primitive solar system materials, suggesting that they must have formed under special conditions not representative of the nebula. It is again emphasized that the Os isotopic compositions of CAIs and chondrites were not affected by the late mobility of Re or Os that resulted in the deviations of some samples from the IIIA iron meteorite isochron. The mean of the distribution of $^{187}\text{Os}/^{188}\text{Os}$ for group I, III, V, and VI CAIs analyzed in this study, including split 4 of a coarse-grained CAI analyzed by Chen et al. (1999), yields a value of 0.12652 ± 28 (Fig. 5a). This value overlaps with data obtained from the CI chondrites Ivuna and Orgueil, and other primitive carbonaceous chondrite bulk rocks (Murchison, Ornans, Allende, and Vigarano), most of which lie in the range 0.1263 to 0.1265 (Fig. 5b, Walker et al., 2001; unpublished data). We conclude that the modern $^{187}\text{Os}/^{188}\text{Os}$ of the bulk solar system must lie within this narrow range and adopt a value of 0.1265, the average of the CI chondrite data and group I, III, V, and VI CAI data. The likely $^{187}\text{Os}/^{188}\text{Os}$ for the solar system is significantly lower than the values for enstatite chondrites, ordinary chondrites, and estimated compositions for the primitive upper mantle of the Earth's mantle (Meisel et al., 1996; 2001; Walker et al., 2001). Although some of these bodies may represent much larger mass fractions than carbonaceous chondrites, they show substantial depletions in lithophile and siderophile volatile elements compared to carbonaceous chondrites (Wänke and Dreibus, 1988; Wasson and Kallemeyn, 1988), and hence, may not be representative of the bulk solar system. Using the isochron parameters for the oldest group of magmatic iron meteorites (IIIA, 4558 ± 12 m.y., Smoliar et al., 1996), the value of 0.1265 for $^{187}\text{Os}/^{188}\text{Os}$ corresponds to a $^{187}\text{Re}/^{188}\text{Os}$ of 0.3964, or a Re/Os weight ratio of 0.0817 for the bulk solar system.

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